



Phase equilibrium for argon clathrate hydrate at the temperatures from 197.6 K to 274.1 K



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ABSTRACT

The phase equilibrium conditions of clathrate hydrate of argon were measured by the isochoric procedure at the temperatures from 197.6 K to 274.1 K. Argon hydrate would have industrial applications including a working medium of the hydrate-based heat pump systems as well as influence the analysis of the past climate change on the Earth. Nevertheless, the equilibrium conditions of argon hydrate were limited in the literatures and not reported below the temperature 264 K. The lowest and the highest measured equilibrium pressure is the pressure 0.825 MPa at the temperature 197.6 K and the pressure 9.881 MPa at the temperature 274.1 K. The equilibrium pressure increases with an increase in temperature. The reliability of the measured equilibrium conditions is supported by the internal consistency of those and the coincidence of the experimentally determined quadruple point (vapor + hydrate + ice + aqueous phases in equilibrium) temperature with the water freezing temperature theoretically predicted. The discussion is given on the comparison of the equilibrium data measured in this study and those reported in the literature.

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1. Introduction

Clathrate hydrate (hereafter abbreviated as hydrate) is an ice-like inclusion compound composed of “host” water molecules and other “guest” substances such as light hydrocarbons, carbon dioxide, nitrogen, and noble gases. Hydrate has several unique characteristics: high gas storage capacity (up to 160 times denser than gas at standard temperature and pressure), large heat of formation/dissociation (up to 1.5 times larger than that of ice per mass), guest selectivity (fractionation between gas and hydrate phases), and “self-preservation” phenomenon (anomalously slow dissociation below the water freezing temperature despite under thermodynamically unstable conditions). Technologies utilizing hydrate were widely proposed, e.g., ozone storage [1], solid carbonated food [2], heat pump/engine [3,4], thermal energy storage as phase change material [5], gas purification [6], and fire extinction [7]. The operation conditions and performance of those technologies are based on the thermophysical properties of hydrate [3]. The measurements of the thermophysical properties can lead to develop hydrate-based technologies previously proposed and to create noble technologies utilizing hydrate.

Hydrate is also occurring in nature [8–10]. An example of hydrate naturally occurs is air hydrate in ice sheets on Antarctica

and Greenland [11,12]. Ancient atmosphere is trapped in ice sheets and is isolated from the contemporary atmosphere. The trapped air is a direct clue of the past climate change. Air bubbles change to air hydrate in the deep ice sheets because low temperature and high pressure in the deep ice sheets is appropriate to form hydrate [13]. Composition of air bubbles in ice sheets changes with hydrate formation due to fractionation of hydrate, that is, N_2/O_2 ratio of air bubbles increases with hydrate formation [14]. Air hydrate in ice cores cannot be neglected to reconstruct the ancient air from bubbles in ice cores.

Hydrate is thermodynamically stable at higher pressures than the phase equilibrium pressure at a given temperature, or at lower temperatures than the equilibrium temperature at a given pressure. Phase equilibrium conditions of air hydrate should be a basis for further understanding of the climate and environment on the Earth. The phase equilibrium conditions of nitrogen hydrate [15], oxygen hydrate [16], $N_2 + O_2$ hydrate (formed from $N_2 + O_2$ gas mixture) [15], and “Air” hydrate (composition was not specified) [16] were measured below the water freezing temperature. The critical size of nucleus and energy barrier for air hydrate were estimated based on the measured equilibrium conditions and hydrate forming conditions in ice sheets [17].

The influence of argon (approx. 0.9 mol% in dry contemporary atmosphere) on the phase equilibrium conditions of air hydrate has been neglected in the previous analysis due to the limitation of measured data. The phase equilibrium pressure of hydrate

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formed from gas mixture is generally lower than a weighted average pressure of simple hydrate (formed from simple guest) forming pressure [18]. The equilibrium conditions of air hydrate should not be estimated by weighted average of those of simple hydrate. In fact, the analysis of air hydrate based on the equilibrium conditions calculated by weighted average of the simple hydrates may lead inaccurate conclusion that some air hydrate exists in the ice sheets under unstable conditions because of “self-preservation” of hydrate [19]. An analysis based on the measured equilibrium conditions of $N_2 + O_2$ hydrate revealed that the air hydrate exists under thermodynamically stable conditions [17]. For further accurate geophysical analysis on the Earth, influence of argon on the phase equilibrium conditions of the air hydrate should be considered because the phase equilibrium pressure of argon hydrate is approximately half lower than that of nitrogen hydrate and oxygen hydrate. The composition of the air bubble gradually changes with formation of hydrate in ice sheets. Statistical-thermodynamics model proposed by van der Waals and Platteeuw (vdW-P model) [18] is a powerful tool to estimate the equilibrium conditions of hydrate at a given thermodynamic state: temperature, pressure, compositions and etc. In vdW-P model, the inter-molecular parameters for the equilibrium condition estimation are generally adjusted to give a good agreement between experimental and predicted equilibrium conditions [20,21]. The phase equilibrium condition measurements of argon hydrate will be useful to estimate the equilibrium conditions of air hydrate in ice sheets that formed from varied air composition and may lead to better understanding for the ice sheets physics. The equilibrium conditions of argon hydrate were limited in the literature and not reported below the temperature 264.3 K [22,23], whereas those of nitrogen hydrate and $N_2 + O_2$ hydrate were measured above the temperature 243 K [15]. In this study, the three-phase (argon-rich vapor + hydrate + ice/aqueous) equilibrium conditions were measured at the temperatures from 197.6 K to 274.1 K. The quadruple point (vapor + hydrate + ice + aqueous) was also determined experimentally.

Table 1
Specification of the materials used in this study.

Chemical name	Chemical formula	Supplier	Purity
Water	H ₂ O	Laboratory made	Electrical conductivity was less than 0.5×10^{-4} S/m
Argon	Ar	Japan Fine Products Co. Ltd.	0.99999 vol fraction was certified

2. Experimental

2.1. Materials

The materials utilized in the experiment are specified in Table 1 with their purities. The distilled water and argon gas were used. The distilled water was deionized prior to the distillation in our laboratory. The electrical conductivity of the distilled water was $<0.5 \times 10^{-4}$ S/m. The argon gas was supplied with 0.99999 vol fraction certificated purity and utilized without further purification in the laboratory.

2.2. Apparatus

Two pressure vessels were used in this study for the phase equilibrium condition measurements dependent on the experimental temperature. The schematic of the pressure vessels is shown in Fig. 1. The pressure vessel was sealed with a stainless-steel V-gasket for $T < 243$ K, whereas sealed with a nitrile rubber O-ring for $T > 243$ K. The reliability of the vessels was confirmed in the previous phase equilibrium condition measurements [15,24–27]. The phase equilibrium conditions were measured by the isochoric procedure through the formation and dissociation of hydrate in the closed pressure vessels [27]. The inner sizes of the vessels were 40 mm diameter and 40 mm height for $T < 243$ K, and 80 mm diameter and 40 mm height for $T > 243$ K. A magnetic stirrer was equipped to agitate the inner fluid, ice and hydrate crystals. The vessels were immersed in temperature-controlled bath filled with ethanol for $T < 243$ K or ethylene glycol aqueous solution for $T > 243$ K. The inner pressure of the vessels was measured by a strain-gauge pressure transducer (model PG-50KU, Kyowa Electric Instruments Co. Ltd., Tokyo, Japan for $P < 5$ MPa; model PG-100KU, Kyowa Electric Instruments Co. Ltd., Tokyo, Japan for $P > 5$ MPa). The estimated uncertainties of the pressure measurements were 17 kPa for $P < 5$ MPa and 18 kPa for $P > 5$ MPa with $k = 2$, where k denotes the coverage factor. A platinum resistance thermometer (Pt-100 Class B, Ichimura Metal Co. Ltd., Tokyo, Japan) was equipped to measure the inner temperature of vapor with the calibration against a Pt-100 reference thermometer (with certificated standard uncertainty 0.03 K, model Rf-100, Electronic Temperature Instrument Ltd., Worthing, UK). The estimated uncertainty of the temperature measurements was 0.15 K with $k = 2$. The sequential pressure and temperature data were acquired by a data logger (model GL820, Graphtec Corporation, Yokohama, Japan).

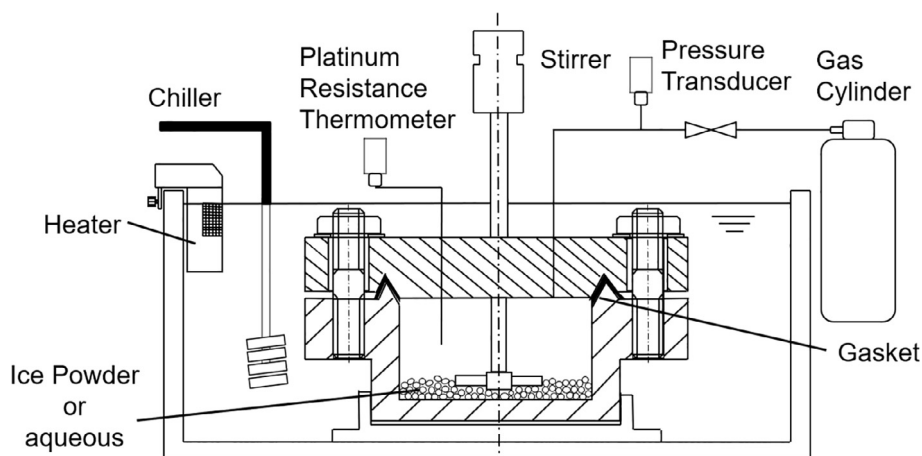


Fig. 1. Schematic of experimental apparatus. Stainless-steel V-gasket and nitrile rubber O-ring were equipped as gasket for $T < 243$ K and $T > 243$ K, respectively.

2.3. Procedure

The three-phase (vapor + hydrate + ice/aqueous) equilibrium conditions were measured by the batch, isochoric procedure [28] in this study. In the isochoric procedure, the phase equilibrium conditions were determined in the closed vessel through the formation and dissociation of hydrate [28]. A typical sequential P versus T diagram during an experimental run in this study is shown in Fig. 2. The reliability of the isochoric procedure was confirmed in the previous studies below and above the water freezing temperature [27]. Before the experiment, ice powder/liquid water was supplied into the vessel and the vessel was sealed with the V-gasket or O-ring. Ice powder was well grained and had 1 mm or smaller diameter for $T < 243$ K or from 1 mm to 2 mm diameter for $243 \text{ K} < T < 270$ K. Ice was formed from the distilled water at 253 K under atmosphere. The mass of ice powder/liquid water was approximate 7 g for $T < 243$ K, 30 g for $243 \text{ K} < T < 270$ K, and 50 g for $T > 270$ K. The mass of ice/liquid water was measured by an electric balance (model GF-3000, A&D Co. Ltd., Tokyo, Japan, with certificated uncertainty of $\pm 0.015 \text{ g}$ ($k = 2$)). To eliminate the air inside the vessel, the vapor in the vessel was discharged to the pressure 10 kPa using vacuum pump and argon gas was supplied into the vessel at the pressure 200 kPa. The inner partial pressure of the air decreased to 0.05 times as a result of one charge and discharge cycle. This cycle was repeated five times and finally the inner partial pressure of the air decreased to the pressure 0.1 Pa or lower. After the elimination of the air in the vessel, argon gas was supplied into the vessel at a prescribed pressure at which hydrate is thermodynamically unstable. Then, the vessel was closed and cooled to form argon hydrate. The pressure inside the vessel was significantly decreased with formation of hydrate because of the large gas uptake into hydrate. After the hydrate formation, the temperature of the system increased stepwise with a step of temperature 0.1 K. The system temperature was kept constant at every temperature step up to the time 48 h until the inside pressure reached to constant. The constant pressure value at a given temperature was recorded and plotted on P versus T plane as shown in Fig. 2. The slope of P versus T trace on P versus T diagram was significantly changed at a temperature in all experimental runs. The

inner pressure increased greatly with an increase in temperature in the presence of hydrate contacting with the vapor because large amount of gas was released from hydrate, whereas the pressure increased slightly in the absence of hydrate contacting with the vapor because the increase in the pressure was chiefly ascribed to the thermal expansion of the inner vapor. All the hydrate contacting with the vapor dissociated at the temperature at which the slope sharply changed and hence the temperature and pressure at that point was considered to be the three-phase (vapor + hydrate + ice/aqueous) equilibrium condition.

The inside pressure did not recover to the initial value when the measurement was performed with ice powder, although the vessel was finally heated to the initial temperature. Such pressure deficiency was observed as well as in the previous measurements coexisting with ice [15,24,25,27]. This deficiency was likely due to the “self-preservation” of hydrate, that is, some amount of hydrate still existed within the ice powders. The remaining hydrate can be considered as isolated from the inner vapor because the inside pressure was stable for the time 72 h after the experimental run. Therefore, we considered that the remaining hydrate within the ice powder did not affect the measurements and their reliability.

In addition to the three-phase (vapor + hydrate + ice/aqueous) equilibrium condition measurements, we performed an experiment to determine the quadruple point in argon + water system independent from the three-phase equilibrium condition measurements. The quadruple point means the four-phase (vapor + hydrate + ice + aqueous) equilibrium condition in argon + water system. According to the Gibbs' phase rule, the degree of freedom of quadruple point is zero. The experimental method was previously utilized to determine the quadruple point [27]. The reliability of the measurements was confirmed by the comparison between the quadruple point temperatures experimentally determined and theoretically estimated water freezing temperature at the quadruple point pressure [27]. The sequential P versus T trace in the quadruple point measurements is shown in Fig. 3. First, a large amount of hydrate was formed at the temperature 273.8 K. After the hydrate formation, the vessel was cooled to form ice. Then, the vessel was heated stepwise with a step of the temperature

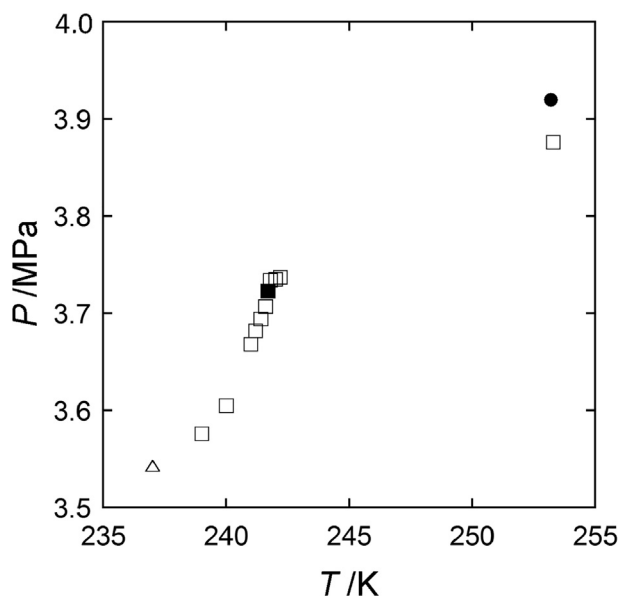


Fig. 2. Typical sequential P versus T diagram during a measurement for the three-phase (vapor + hydrate + ice) equilibrium conditions. ●, Initial; Δ, argon hydrate formation; □, stepwise heating process; ■, obtained phase equilibrium conditions.

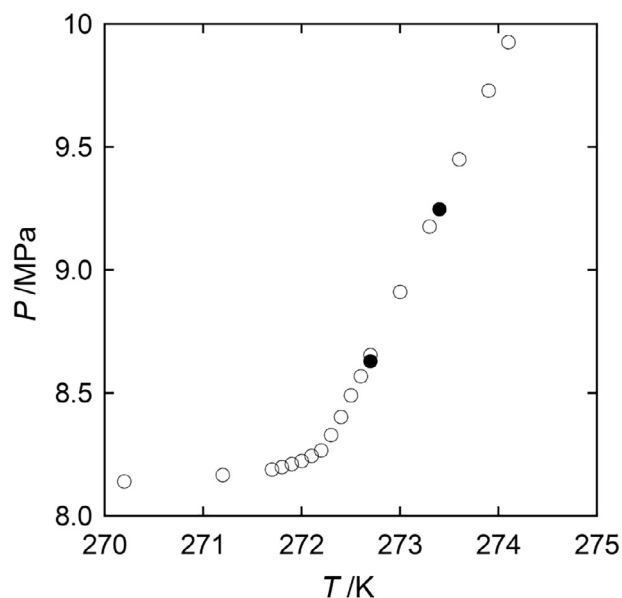


Fig. 3. Sequential P versus T trace in the quadruple point measurement. ○, sequential data; ●, vapor + hydrate + aqueous equilibrium conditions in this study.

Table 2Sequential P - T data below and above the quadruple point in argon + water system.

T/K^a	P/MPa^b
270.2	8.141
271.2	8.167
271.7	8.189
271.8	8.199
271.9	8.212
272.0	8.224
272.1	8.245
272.2	8.267 ^c
272.3	8.329
272.4	8.403
272.5	8.490
272.6	8.568
272.7	8.655
273.0	8.912
273.3	9.176
273.6	9.450
273.9	9.730
274.1	9.926

^a $U(T) = 0.15 \text{ K}$ ($k = 2$).^b $U(P) = 0.018 \text{ MPa}$ ($k = 2$).^c Quadruple point experimentally determined.

0.1 K. The system temperature was kept constant until the system pressure reached to stable at every temperature step. The stable pressure value at each temperature was recorded as specified in Table 2 and plotted as shown in Fig. 3. It is reported that this sequential P versus T trace was in good agreement with the three-phase equilibrium conditions in the two-component hydrate forming system [27]. The slope of the P versus T trace on P versus T plane sharply changed at the quadruple point with the change of equilibrium state (with ice or with aqueous). Therefore, we considered that the point at which the slope sharply changed on P versus T plane was the quadruple point in argon + water system.

3. Results and discussion

The three-phase (vapor + hydrate + ice/aqueous) equilibrium conditions were measured at the temperatures from 197.6 K to 274.1 K. The measured equilibrium conditions are specified in Table 3 and shown in Fig. 4 with the literature data. The lowest equilibrium pressure is the pressure 0.825 MPa at the temperature 197.6 K, and the highest equilibrium pressure is the pressure 9.881 MPa at the temperature 274.1 K. The equilibrium pressure increases with an increase in temperature at the temperatures

Table 3

Three-phase (vapor + hydrate + ice/aqueous) equilibrium conditions in argon + water system.

T/K^a	P/MPa	Phases in equilibrium
197.6	0.825 ^b	vapor + hydrate + ice
203.0	1.024 ^b	vapor + hydrate + ice
211.4	1.410 ^b	vapor + hydrate + ice
222.6	2.056 ^b	vapor + hydrate + ice
229.1	2.509 ^b	vapor + hydrate + ice
241.4	3.691 ^b	vapor + hydrate + ice
241.7	3.723 ^b	vapor + hydrate + ice
253.1	5.062 ^c	vapor + hydrate + ice
261.0	6.355 ^c	vapor + hydrate + ice
266.2	7.158 ^c	vapor + hydrate + ice
269.7	7.807 ^c	vapor + hydrate + ice
272.7	8.629 ^c	vapor + hydrate + aqueous
273.4	9.247 ^c	vapor + hydrate + aqueous
274.1	9.881 ^c	vapor + hydrate + aqueous

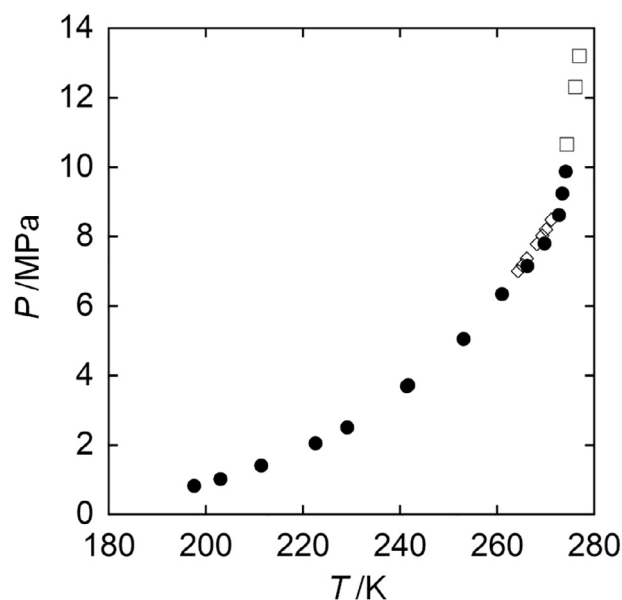
^a $U(T) = 0.15 \text{ K}$ ($k = 2$).^b $U(P) = 0.017 \text{ MPa}$ ($k = 2$).^c $U(P) = 0.018 \text{ MPa}$ ($k = 2$).

Fig. 4. Three-phase (vapor + hydrate + ice/aqueous) equilibrium conditions in argon + water system. ●, This study; ◇, Mohammadi & Richon [22]; □, Saito et al., [23].

from 197.6 K to 274.1 K. The measured equilibrium data are aligned on two smooth curves for below and above the temperature 272 K, respectively. The slope of the measured equilibrium data changed sharply around the temperature 272 K. This change of the slope can be ascribed to the change of the water phase in equilibrium, solid ice or liquid aqueous, according to Clapeyron equation as follows:

$$\frac{\partial P}{\partial T} = \frac{\Delta h}{T \Delta v} \quad (1)$$

where P and T denotes the equilibrium pressure and temperature, Δh is the formation/dissociation enthalpy of hydrate per mol of guest, Δv is the volume changes that take place due to the phase change. Δh is significantly changed with the change of the water phases in equilibrium [29]. The slope of the equilibrium conditions on P versus T plane is changed around the temperature 272 K below and above the water freezing temperature. Therefore, the alignment on two curves is thermodynamically reasonable. This supports the internal consistency and reliability of the measured equilibrium conditions.

The phase equilibrium conditions were measured duplicately from the same initial conditions: $P = 3.920 \pm 0.017 \text{ MPa}$ at $T = 253.2 \pm 0.15 \text{ K}$ with the ice mass $6.603 \pm 0.015 \text{ g}$ for the first run and $P = 3.906 \pm 0.017 \text{ MPa}$ at $T = 253.2 \pm 0.15 \text{ K}$ with the ice mass $6.610 \pm 0.015 \text{ g}$ for the second run ($k = 2$). The sequential P versus T data during the duplicate experiments are shown in Fig. 5. The three-phase equilibrium conditions were determined to be $P = 3.723 \pm 0.017 \text{ MPa}$ at $T = 241.7 \pm 0.15 \text{ K}$ from the first run and $P = 3.691 \pm 0.017 \text{ MPa}$ at $T = 241.4 \pm 0.15 \text{ K}$ from the second run ($k = 2$). These equilibrium conditions mutually coincided within the uncertainties of the pressure and temperature measurements. This coincidence supports the reproducibility of the measured equilibrium conditions.

Although the reliability and reproducibility of the measured equilibrium conditions are supported, the measured equilibrium conditions are inconsistent with those in the literature [22]. For instance, the equilibrium pressure was measured to be $P = 7.158 \pm 0.018 \text{ MPa}$ at $T = 266.2 \pm 0.15 \text{ K}$ in this study, whereas $P = 7.37 \pm 0.02 \text{ MPa}$ at $T = 266.1 \pm 0.1 \text{ K}$ in the previous study [22], or the

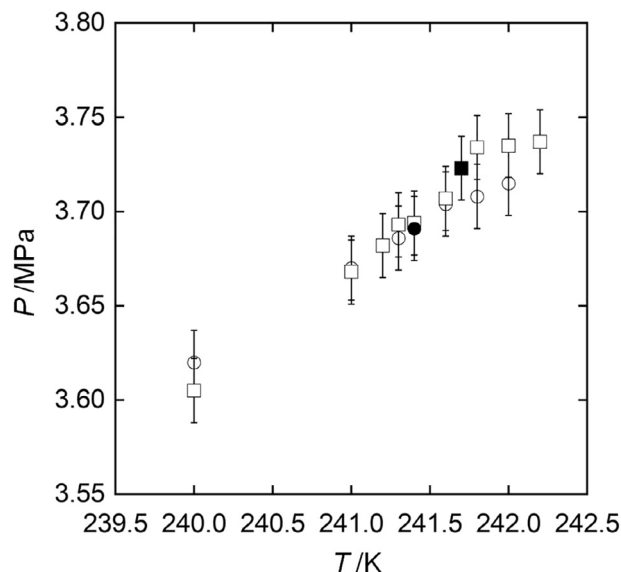


Fig. 5. Sequential P versus T diagram in duplicate measurements. (■, □), first run; (●, ○), second run; (■, ●), obtained equilibrium conditions. The error bars indicate the extended uncertainty of pressure measurements ($k = 2$).

equilibrium temperature was measured to be $T = 269.7 \pm 0.15$ K at $P = 7.807 \pm 0.018$ MPa in this study, whereas $T = 268.2 \pm 0.1$ K at $P = 7.79 \pm 0.02$ MPa in the previous study [22]. The deviations between the equilibrium conditions measured in this study and in the literature [22] exceeded the mutual uncertainties of the measurements despite at the same temperature or pressure.

To compare the measured equilibrium data with the literature data [22,23], the equilibrium data were plotted on the $\ln P$ versus $1/T$ plane as shown in Fig. 6. The measured equilibrium data are aligned on two straight lines on $\ln P$ versus $1/T$ plane. This alignment is consistent with Clausius-Clapeyron equation as follows:

$$\frac{d(\ln P)}{d(1/T)} = -\frac{\Delta h}{zR} \quad (2)$$

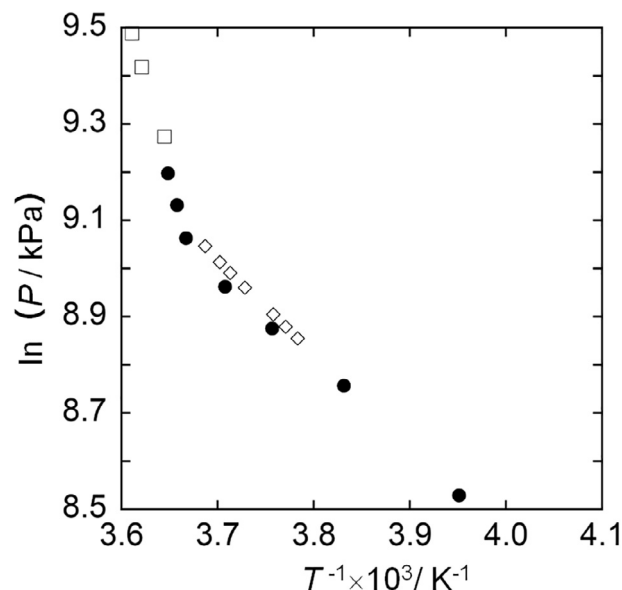


Fig. 6. Three-phase (vapor + hydrate + ice/aqueous) equilibrium conditions in argon + water system replotted on the $\ln P$ versus $1/T$ plane. ●, This study; ●, Mohammadi & Richon [22]; □, Saito et al., [23].

where P and T denote the equilibrium pressure and temperature, Δh is the formation/dissociation enthalpy of hydrate per mol of guest, z is the compressibility factor at P and T , and R is universal gas constant. The pressure and temperature range shown in Fig. 6 is from $P = 6.002$ MPa ($\ln(P/\text{kPa}) = 8.5$) to $P = 13.360$ MPa ($\ln(P/\text{kPa}) = 9.5$) and from $T = 277.78$ K (0.0036 K $^{-1}$) to $T = 243.90$ K (0.0041 K $^{-1}$). z is 0.935 at $T = 261.0$ K and $P = 6.355$ MPa, and 0.928 at $T = 274.1$ K and $P = 9.881$ MPa. z can be assumed to be constant at the P and T range shown in Fig. 6. The straight alignment indicates that Δh is respectively constant below and above the water freezing point at P and T range shown in Fig. 6. The slopes of the correlation lines of the measured equilibrium conditions are -1658.6 K below the water freezing point (for gentle line) and -7233.8 K above the water freezing point (for steep line). The slopes of the literature data are -1970.9 K [22] below the water freezing point, and -6342.9 K [23] above the water freezing point. The values of the slopes of the literature data are 18% greater and 12% smaller than those in this study below and above the water freezing point. This inconsistency of the slopes indicates that the measured equilibrium conditions are significantly inconsistent with those in the literature.

As discussed above, the measured equilibrium conditions are inconsistent with those in the literature. The quadruple point (vapor + hydrate + ice + aqueous) was experimentally determined to further evaluate the reliability of the measured equilibrium conditions. The quadruple point was experimentally determined to be $P = 8.267$ MPa at $T = 272.2$ K as shown in Fig. 3 and Table 4 with that estimated from the literature data and theoretically calculated quadruple point temperatures. The sequential P versus T trace was in good agreement with the measured equilibrium conditions and in good continuity below and above the quadruple point as shown in Fig. 3. As ice and aqueous are in equilibrium at the quadruple point, the quadruple point temperature is theoretically equal to the water freezing temperature under the quadruple point pressure. It was previously reported that the quadruple point temperature experimentally determined was in good agreement with the calculated water freezing point temperature in various hydrate forming systems [27,30]. The solubility of argon gas was calculated to be 0.187 mol/kg at the quadruple point based on the Henry's constant on NIST Chemistry Webbook [31]. The depression of the water freezing point by the dissolved argon gas was estimated to be 0.35 K at $P = 8.267$ MPa. The water freezing point temperature is also depressed by pressure [32]. The depression by pressure is 0.36 K at $P = 5$ MPa and 0.74 K at $P = 10$ MPa [32]. The depression by the pressure was estimated to be 0.61 K at $P = 8.267$ MPa with the assumption that the depression linearly depends on the pressure at the pressure from 0 MPa to 10 MPa. Overall, the water freezing temperature at the quadruple point pressure was calculated to be $T = 272.19$ K. In this study, the quadruple point temperature experimentally determined is in good agreement with the calculated water freezing temperature at the quadruple point

Table 4

The quadruple point (vapor + hydrate + ice + aqueous) in argon + water system, and theoretical calculations for the water freezing temperature under the quadruple point pressure.

T_{exp}/K	P/MPa	$T_{\text{theo}}/\text{K}^a$	Ref.
272.2 ^b	8.267 ^b	272.19	This study
271.9 ^c	8.622 ^c	272.15	Mohamamdi Saito et al.

^a The temperature at quadruple point was calculated from the freezing point depression of water because of pressure and dissolving argon gas at determined equilibrium pressure.

^b The quadruple point was determined from sequential heating process.

^c The quadruple point was deduced from the cross point on P versus T plane of the extrapolation of the equilibrium condition data in the literatures.

pressure. This thermodynamic coincidence supports the reliability of the measured phase equilibrium conditions. The quadruple point was estimated to be $P = 8.622$ MPa at $T = 271.9$ K by the extrapolation of the equilibrium conditions in the literature [22,23]. The quadruple point estimated from the literature data is inconsistent with that experimentally determined in this study. The water freezing temperature at that quadruple point was calculated to be $T = 272.15$ K. This calculated temperature is 0.25 K higher than the estimated quadruple point temperature from the literature data although the quadruple point temperature is in good agreement with the calculated water freezing temperature in this study and in the previous studies [27,30]. As discussed above, it is shown that the phase equilibrium conditions measured in this study are thermodynamically consistent, whereas those in the literatures [22,23] are thermodynamically inconsistent. Thermodynamic consistency supports the reliability of the phase equilibrium conditions measured in this study.

4. Conclusions

The three-phase (vapor + hydrate + ice/aqueous) equilibrium conditions were measured at the temperatures from 197.6 K to 274.1 K in argon + water system. The equilibrium conditions were newly measured and reported below the temperature 264 K. The reliability of the measured equilibrium data is supported by thermodynamic consistency; the internal consistency of the measured equilibrium data and the agreement of the experimentally determined quadruple point (vapor + hydrate + ice + aqueous phases in equilibrium) temperature with the water freezing temperature theoretically predicted. For the development of hydrate-based heat-pump system and other technologies and further accurate understanding of the environment on the Earth, further measurements of the phase equilibrium conditions in argon hydrate forming system are desired.

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